COATINGS. ENAMELS

COORDINATION STATE OF BORON AND ALUMINUM IN LOW-ALKALI ALUMINOBOROSILICATE GLASSES

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The structure of aluminoborosilicate glasses is considered. It is found that the coordination states of boron and aluminum in glasses may vary depending on the composition, which has a perceptible effect on the properties of glaze glasses. Significant discrepancies were found between the experimental and calculated TCLE values of such glasses, which is due to a changed content of four-coordination boron and the emergence of six-coordination aluminum. Considering these data, it is possible to predict the physicochemical properties of glaze glasses.

Aluminoborosilicate glasses are widely used as glazes for ceramics materials and glass seals in engineering. At present boron-containing glasses and glazes are objects of numerous studies [1 – 4]. This interest is related to the structural specifics of these glasses depending on the coordination transformations of boron and aluminum, which makes it possible to use them as model systems for studying physicochemical properties.

Discrepancies between the experimental and calculated TCLE values have been found in aluminoborosilicate glasses, which is related to changes in the coordination state of boron and aluminum [5]. The study of the correlation between the TCLE and the coordination state of boron and aluminum in glaze glasses was performed on four compositions of glasses of the system $K_2O – Na_2O – CaO – Al_2O_3 – B_2O_3 – SiO_2$ (Table 1).

Glasses were melted from chemical reactants of grades "chemically pure" and "pure for analysis" in corundum crucibles; the reference compositions were melted in platinum crucibles. The melting temperature was 1200 – 1250°C. Glasses of compositions 2 – 4 are derived from glass 1 and are obtained by additionally introducing B_2O_3 (above 100 wt.%): 26% in glass 2, 40% in glass 3, and 50% in glass 4.

The x-ray spectral studies of the state of boron were performed using a RSM-500 monochromatic spectrometer. The device involved a copper anode (operating regime of the tube: $I = 110$ mA, $U = 8$ kV), a diffraction grid with a curvature radius of 2 m, and a focusing mirror with a polystyrene coating. The sample was positioned at an angle of 12° with respect to x-ray beam. The spectra were recorded at points and connected to a printer. The x-ray spectral analysis of the state of aluminum ions was implemented on a VRA-20R spectrometer with a tube with a chromium anode (regime: $I = 35$ mA, $U = 40$ kW).

The TCLEs of glasses were determined on a DKV-5a dilatometer in a temperature interval of 20 – 300°C; the calculation of the TCLE was performed in accordance with A. A. Appen's method [6].

It can be seen in Fig. 1 that the difference between the experimental and the calculated dependences of the TCLE of the glasses considered grows significantly passing to high-boron compositions: for glasses with a molar content of B_2O_3 not more than 40% (glasses 1 and 2), the difference between the experimental and estimated values is approximately equal and does not exceed 2.5%, which agrees with the published data, whereas for glass 4 containing about 60% B_2O_3 this difference is nearly 100%. The reason for this sharp increment in the discrepancy between the calculated

TABLE 1

Composi-tion	Molar content (from synthesis), %					
	Na$_2$O	K$_2$O	CaO	Al$_2$O$_3$	B$_2$O$_3$	SiO$_2$
1	5.8	1.7	11.0	7.9	17.1	56.5
2	4.4	1.3	8.3	5.9	37.6	42.5
3	3.4	1.0	6.7	5.1	51.8	32.0
4	2.7	0.7	5.4	4.1	58.5	28.6

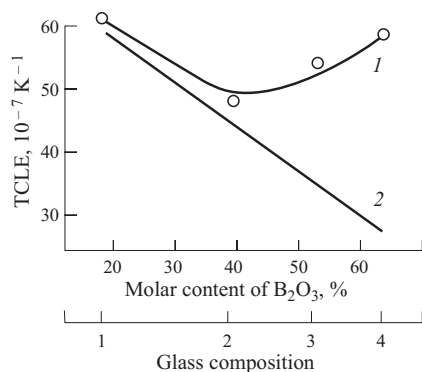[1] Kazan State Power University, Kazan, Russia; Kazan State Architecture-and-Construction Academy, Kazan, Russia.

Fig. 1. Experimental (*1*) and calculated (*2*) dependences of TCLE of glasses considered.

Fig. 2. VK spectra of quantum efficiency of glasses (*a*) and dependence of the parameter S_1/S_2 on N_4 (*b*).

and the experimental data may be a modification of structure not taken into account in the calculation, in particular, a modification of the coordination state of boron and aluminum atoms.

The most typical glasses, i.e., the ones with the minimum (glass 2) and the maximum (glass 4) discrepancies between the experimental and calculated TCLEs, were selected for further research. The polymer lattices of the glasses considered contain two independent components: the borate component mainly made up by triangles [BO_3] polymerized in rings and the silicate component that may contain tetrahedra [AlO_4] and [BO_4]. The alkali and alkali-earth oxides contained in glass apparently do not play a depolymerizing role. With increasing B_2O_3 content and decreasing amount of alkalis, the share of the borate component grows, whereas the content of boron-oxygen tetrahedra decreases.

The quantitative content of boron in the four-coordination state in glasses 2 and 4 was determined by processing K-spectra of the quantum efficiency of boron atoms: long VK and medium SKV (Fig. 2). The spectra of glasses 2 and 4 are characterized by the presence of an intense isolated peak *a* — 193.3 – 193.9 eV and a high-energy band consisting of weakly resolved maxima (eV): *b*) very weak, 196.8 – 197.2; *c*) 200.5 – 200.9; *d*) 201.1 – 201.8; *e*) 202.0 – 202.8; *f*) 203.0 – 203.8; *g*) weak, 204.1 – 205.3. These maxima are clearly visible in the spectra of the model minerals with a known coordination number of boron (B_2O_3 with coordination 3 and pinnoite with coordination 4). The spectra of the borates containing boron atoms in the four-coordination state show a prevalence of maxima *c* and *d* over maxima *e* and *f*. When the coordination number of boron is equal to 3, their intensity drops to a very low value, whereas the maxima *e* and *f* become the main ones.

To identify the role of boron in four-coordination N_4, the ratio of integral intensities in the bands 198.0 – 200.5 and 201.5 – 204.0 eV determined via the surface areas S_1 and S_2 was used (Fig. 2*a*). This method is considered in more detail in [7, 8]. Figure 2*b* shows the final correlation dependence $N_4 = f(S_1/S_2)$ used in the present study. The value N_4 for glass 2 is $9 \pm 5\%$, i.e., the majority (around 90%) of the bo-
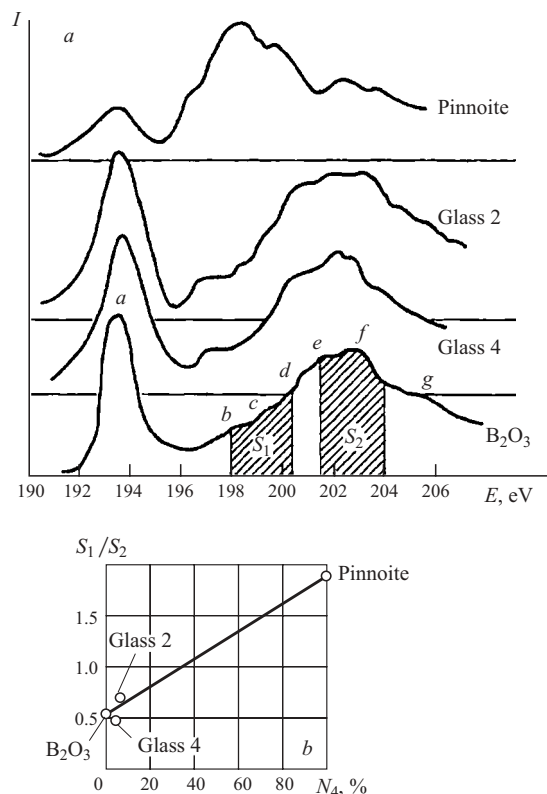
ron atoms are three-coordinated and incorporated in glass in the form of a three-dimensional lattice consisting of triangles [BO_3]. For glass 4 the value N_4 drops to zero, and boron in the four-coordination state is virtually absent.

Small differences in the fine structure of the spectra of the glasses considered in the range of the maxima *a*, *b* and *c* can be explained by the fact that in this case the effect of the second coordination sphere of boron atoms is presumably manifested in the VK – SKV spectra in the form of small disturbance of the structure of molecular orbitals determined by the coordination (i.e., the symmetry of the ligand field). Analyzing the intensity of the maxima *b* and *c*, it can be assumed that the effective charge on the boron atom, near which the Na^+ and K^+ cations are located, is somewhat greater than in the case of a boron atom bonded with calcium via oxygen.

The coordination state of aluminum is determined by processing $AlK_{\alpha1,2}$ emission spectra. The energy shifts of $AlK_{\alpha1,2}$ lines were determined based on the shift of the gravity center of the doublet with respect to its position for metallic aluminum ($\Delta EAlK_{\alpha1,2}$). Analysis of the values $\Delta EAlK_{\alpha1,2}$ for glasses 2 and 4 indicated that the energy shift grows from 0.18 eV for glass 2 to 0.28 eV for glass 4. It is known that the range of variation of the parameter $\Delta EAlK_{\alpha1,2}$ from 0.11 to 0.24 eV is characteristic of the tetrahedral environment of aluminum and from 0.39 to 0.50 eV typical of the octahedral environment [9, 10]. Hence the increased energy shift in the

gravity center of the $AlK_{\alpha1,2}$ line in transition from glass 2 to glass 4 can be interpreted as due to the formation of a certain number of six-coordination aluminum. Assuming that aluminum in glass 2 is totally four-coordinated, it can be assumed with a certain reservation that in glass 4 about one-quarter of the total number of aluminum atoms are six-coordinated.

Considering that sodium cations are consumed in the formation of a crystalline microphase represented by sodium tetraborate and leave the vitreous phase, potassium and calcium cations should play an active role in the compensation of the charges on the tetrahedra $[BO_4]$ and $[AlO_4]$. It is believed that aluminum forms a tetrahedron more easily than boron does and the tetrahedron $[AlO_4]$ is more stable than the tetrahedron $[BO_4]$. Accordingly, oxygen bonded to the cations of alkali (or alkali-earth) metals in aluminoborosilicate glasses should be primarily consumed in the formation of tetrahedra $[AlO_4]$, even in the conversion of boron into coordination 3.

The presence of small quantities of $[BO_4]$ (approximately 9%) in glass 2 is of interest, since aluminum in this glass-forming system (according to the data in [6]) should gather cations to neutralize the excessive charge on its tetrahedra. However, even the total number of alkali oxide ions is insufficient for the conversion of aluminum from the six-coordinated to the four-coordinated state, the more so since there should be no free cations for the formation of tetrahedra $[BO_4]$. Consequently, the compensation of the charge in the glasses considered should be mainly implemented by calcium cations due to the formation of calcium-borate and calcium-aluminate complexes.

The lattice rearrangement in passing from glass 2 to glass 4 should affect the structure-sensitive physicochemical properties of glasses in this system. The discrepancy between the experimental and calculated TCLE values in glasses 5 and 4 can be explained by the change of the share of four-coordination boron, the emergence of six-coordination aluminum, the formation of calcium-borate and calcium-aluminate complexes, and general loosening of the polymer structure. Assuming that the deviation of the experimental TCLE values of glasses 3 and 4 from the TCLEs calculated by the standard method [6] is caused only by a modified coordination of boron and aluminum atoms, we calculated the TCLE for boundary glasses 2 and 4 taking into account these modification. The equation of I. D. Tykachinskii was used [10] and the following TCLE values were applied for B_2O_3 and Al_2O_3 depending on their structural state ($10^{-7} K^{-1}$): 150 for BO_3, 100 for BO_4, 30 for AlO_4, and 150 for AlO_6. The

calculated TCLE value of glass 2 was $41.8 \times 10^{-7} K^{-1}$, and that of glass 4 was $66.7 \times 10^{-7} K^{-1}$. This is significantly closer to the experimental data (Fig. 1); for glass 4 the discrepancy between the calculated and experimental values decreases approximately from 30×10^{-7} to $8 \times 10^{-7} K^{-1}$.

Thus, the discrepancy between the experimental TCLE values and the TCLEs calculated according to A. A. Appen's method can be decreased by taking into account the equilibrium $[BO_3] \leftrightarrow [BO_4]$ and $[AlO_4] \leftrightarrow [AlO_6]$ using the quantitative estimate of the content of the four-coordinated boron and six-coordinated aluminum specified above. The control calculations of TCLEs taking into account the relative quantities of BO_4 and AlO_6 show good agreement with the experimental data, which can produce a positive result in practical application of aluminoborosilicate glasses and glazes and prevent an error in selecting glaze glasses and their coordination with the ceramic substrate.

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